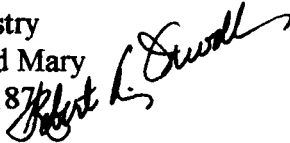


To: Ms. Yolanda White-Woolaston
Tessada & Associates, Inc.
Mail Stop 126, Building 1195B Room 209
NASA Langley Research Center
Hampton, VA 23681

Dr. John W. Connell
Advanced Materials and Processing Branch
Mail Stop 226
NASA Langley Research Center
Hampton, VA 23681-2199

Center for AeroSpace Information (CASI)
7121 Standard Drive
Hanover, MD 21076-1320
Attn: Accessioning Department

From: Robert A. Orwoll
Department of Chemistry
College of William and Mary
Williamsburg, VA 23187



Date: September 30, 2005

Please find enclosed the Final Summary of Research for NASA Grant #NAG-1-02109

Cc: Mr. Mark Roberts
Director, Grants Fiscal Administration
College of William and Mary

Polyimide-Clay Composite Materials for Space Application

FINAL SUMMARY OF RESEARCH REPORT NASA NAG-1-02109

(William and Mary #301641)

Dates: August 2002 - June 2004

Amount: \$19,438

NASA Technical Officer: John Connell

Principal Investigator: Robert A. Orwoll

Address: Department of Chemistry
College of William and Mary
P.O. Box 8795
Williamsburg, VA 23187-8795

Polyimide-Clay Composite Materials for Space Application Final Summary of Research Report

The work described here was funded with NASA grant NAG-1-02109 (William and Mary account #3011641).

The introduction of nanometer-sized clay particles into a polyimide matrix has been shown to enhance the physical properties of specific polymer systems. The clay comprises large stacked platelets of the oxides of aluminum and silicon. These sheets have long dimensions on the order of tenths of a micrometer and thicknesses of several nanometers. Homogeneous dispersion of the clay platelets in the polymer matrix is necessary to achieve those enhancements in polymer properties. Natural montmorillonite with the empirical formula $\text{Na}_{0.33}\text{Mg}_{0.33}\text{Al}_{1.67}(\text{OH})_2(\text{Si}_4\text{O}_{10})$ contains exchangeable inorganic cations. The clay lamellae stack together with the positive sodium ions situated between the surfaces of the individual sheets to balance negatively charged oxygen atoms that are on the surfaces of the sheets. These surface charges contribute to strong electrostatic forces which hold the sheets together tightly. Exfoliation can be accomplished only with unusual measures.

In preparing clay nanocomposites, we have taken two steps to try to reduce these interlamellar forces in order to promote the separation (exfoliation) of the sheets and the dispersion of the individual clay particles throughout the organic polymer matrix. In the first step, some of the surface Na^+ ions are replaced with Li^+ ions. Unlike sodium cations, the lithium cations migrate into the interior of the lamellae when the system is heated. Their departure from the surface reduces the surface charge and therefore the attractive forces between the sheets. The loss of alkali metal cations from the surface can be measured as the cation exchange capacity (CEC) of the clay. For example, we found that the CEC of montmorillonite clay was reduced by almost two thirds by treating it with lithium ions and heating to 250°C for 24 hr. Lesser heating has a smaller effect on the CEC. X-ray diffraction measurements show that the *d*-spacing decreased from *ca.* 1.34 to 0.97 nm, apparently a consequence of a collapse of the clay layers. We observed that the *d*-spacing can be varied by altering the heat treatment.

In the second part of our effort to reduce the interlamellar forces, the remaining inorganic surface cations were replaced by the trimethylphenylammonium ion (TMPA), the biphenyltrimethylammonium ion (BTMA), or the tetraphenylphosphonium ion (TPP). These organo-amines or phosphine gave the inorganic surface of the lamellae an organic coating to render the clay more compatible with the organic polymer. The interlayer spacing in the clay as deduced from X-ray diffraction varied with the organic ion. The aromatic surfactants used in this study showed improved thermal stability when compared with aliphatic surfactants.

The clay nanocomposites were then prepared by mixing small amounts (*e.g.*, 3 wt-% of total solids) of the surfactant-modified clay with a solution of a monomer pair such as 4,4'-oxydianiline (ODA) + 3,3',4,4'-biphenyltetracarboxylic dianhydride (BTDA). The mixture was shaken vigorously to encourage penetration of the monomers into the interlayer spacing of the

clay. The resulting clay-loaded polyamic acid was cast into a film and then imidized by subjecting it to temperatures up to 300°C. The polyimide nanocomposites prepared in this way showed improved tensile moduli over nanocomposites prepared with unmodified montmorillonite. This was especially true for the ODA-BTDA polyimide prepared with TPP-treated clay. X-ray diffraction measurements on this film showed no peaks, an observation consistent with successful intercalation or exfoliation of the clay into the polyimide.

The ODA-BTDA polyimide was also prepared with clays that had been modified with the BTMA and TPP ions as well as with the unmodified clay. A similar series of studies was made with the polyimide product of 1,3-bis(3-aminophenoxy)benzene (APB) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA). In many instances, the X-ray diffraction pattern of each APB-BPDA polyimide containing modified clay differed considerably from the diffraction pattern of the corresponding ODA-BTDA film. This observation suggests that the clays interact with the two polymers differently.

In another series of studies, montmorillonite clay was treated with lithium ions at different temperatures so as to yield a series of clays with varying reduced charges. These clays were then treated with the doubly protonated APB, *i.e.*, the H_2APB^{++} ion, with the intention of exchanging the alkali metal ions on the surface of the clay platelets with the H_2APB^{++} monomer which could then participate in the *in situ* polymerization with BPDA and additional APB monomer. Good dispersions of the clay in the APB-BPDA polyimide were observed using both X-ray diffraction and transmission electron microscopy at clay loadings of 3, 5, and 8 wt-%. Clays whose CEC had been adjusted by heating at 130°C for 24 hr. appeared to have been dispersed most completely. The moduli of the nanocomposites increased with increasing clay loadings, while both the strength and elongation decreased.

In a third aspect of these studies, an aromatic organo-cation with a quaternary ammonium ion at one end and a free amine at the other end was successfully synthesized. Organoclays modified with this cation did not show improved dispersion in APB-BPDA films than the clays modified with H_2APB^{++} . However, these studies were not completed and final conclusions cannot be drawn.

This work supported the research of three William and Mary undergraduates: James Calhoon, Janine Ladislaw, and Barbara Besal.

Details of this work and the techniques employed are available from

“Preparation and Characterization of Polyimide Nanocomposites,” J. F. Cahoon, Honor Thesis, Department of Chemistry, College of William and Mary, May 2003;

“Polyimide Nanocomposites Prepared with a Novel Aromatic Surfactant,” D. M. Delozier, R. A. Orwoll, J. F. Cahoon, J. S. Ladislaw, J. G. Smith, and J. W. Connell, *High Performance Polymers*, **15**, 329 (2003).